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REACTION OF REFRACTORY NOZZLE MATERIALS WITH ZIRCON SANDS AND BOREFIL AT ELEVATED TEMPERATURES

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REACTION OF REFRACTORY NOZZLE MATERIALS WITH ZIRCON SANDS AND BOREFIL AT ELEVATED TEMPERATURES

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ABSTRACT

Reaction between refractory nozzles for VOD ladles and zircon packing sands lead to nozzle blockage resulting in lost production. This paper reports reactions between a variety of refractory materials in contact with the zircon sands.

RÉACTION ENTRE ORIFICES DE COULÉE RÉFRACTAIRES ET SABLES DE ZIRCON

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RÉSUMÉ

Les orifices de poche de coulée en matières réfractaires réagissent avec les sables de garnissage à base de zircon et se bloquent, ce qui entraîne une perte de production. La communication traite de réactions qui se produisent entre différentes matières réfractaires et les sables de zircon.

INTRODUCTION

The increasing demands imposed on refractories by higher refining temperatures, longer holding times and more corrosive alloys and slags make it necessary to seek alternative refractories for use in ladle systems as the conventional refractories currently used are either unreliable or inadequate. In casting heat-resistant, titanium bearing No. 409 stainless steel at Atlas Steels Company, Tracy, Quebec, severe blockage of the nozzle of the ladles has been encountered. It has been postulated that the blockage may be due to the following factors:

(a) reaction between molten metal and the refractory nozzle,
(b) combined reaction of molten steel and slag with the refractory nozzle,
(c) reaction between the protective packing sand and the refractory nozzle.

The reactions of the metal and combined metal-slag systems with the mullite nozzle materials in current use are being examined in CANMET. Preliminary results have shown that the degradation of the mullite nozzles is due to chemical corrosion by either metal and/or metal-slag in contact with the refractories at high temperatures. In addition, tests are also being conducted to determine the performance of selected alternative materials: alumina, spinels and periclase, in contact with molten metal and mixed steel-slag systems.

A trace of zirconium was detected by EDXR (Energy Dispersive X-ray) analysis in the reacted zone of a blocked mullite nozzle, indicating that reaction between the mullite and the zircon sand used for packing the nozzle may also have occurred. The use of packing sands in the sliding-gate system is well known, however the interaction between the zircon sand and different refractories at high temperatures has not been documented in the literature (1). This report describes the investigations undertaken to determine the performance of the currently used and potential alternative refractories in contact with the zircon sands used to protect the nozzles during secondary steel making processes conducted in the VOD ladles at the company's Tracy plant. The work was completed under Cost Recovery Job 025180, funded under the department's START program.

EXPERIMENTAL

MATERIALS

(a) Refractory materials

The chemical compositions of the refractories evaluated for stability in contact with the zircon sands are given in Table 1. There are four major types of refractories, based on mullite, alumina, spinel and periclase compositions. Two classes of mullite refractories are represented, one with a conventional sintered clay bond (MES), the other phosphate bonded (MP). Similarly, the two alumina materials are respectively ethyl silicate bonded (AT2D) and phosphate bonded (HIAPB). The spinel materials represent two compositions differing in the proportions of spinel and magnesia. The periclase material is a densely sintered magnesia. All the samples were provided by the company's supplier as representative of commercially available nozzles.

(b) Packing sands

Two types of packing materials in current use were supplied by the company, to examine their compatibility with the refractory materials.

Type I is fine grained zircon sand of light brown to purple colour. The grain size is in the 150 to 300 μm range.

Type II material is known commercially as "Borefil". The material is in the form of whitish pellets varying from 1 to 3 mm in diameter, which appear to be sintered zircon aggregates.

Apart from the difference in physical appearance, and the obvious traces of impurities responsible for the colour difference, both materials were shown by X-ray diffraction to consist essentially of zircon (Zr_2SiO_4).

(c) Metal

The composition of 409 stainless steel is shown in Table 2.

CUP TESTS

The behaviour of the refractories in simultaneous contact with each packing material and 409 stainless steel was examined at high temperatures in vacuum, using the cup-test method. Initial tests were conducted at normal teeming temperatures (1570°C, 2860°F) for 45 minutes. Subsequently, at the request of the company, additional tests were made at 1716°C

(3120°F) for 45 minutes. The latest available phase data (2) indicate that zircon dissociates at 1676°C to tetragonal ZrO_2 and cristobalite (SiO_2), with the first siliceous liquid phase appearing at 1687°C. These temperatures are below those that might conceivably be seen by the ladle nozzle during oxygen blowing.

The refractory materials were cut into small blocks of approximaely 3.6 cm in diameter by 3.6 cm high. A hole of 1.3 cm diameter by 3.0 cm depth was core drilled at the centre of each block and was then packed, first with 6 g of the sand and then with 2 g of metal shavings on top. The refractory crucible and its contents was contained inside a molybdenum safety crucible, in turn placed inside of a graphite resistance furnace operated under vacuum. Prior to heating the test sample, the furnace was evacuated to a vacuum of 0.15 Pa, then the furnace temperature was increased to the desired test temperature. In all cases, the sample was kept at the test temperature for a period of 45 minutes. Upon completion of the test, the furnace was allowed to cool under vacuum to room temperature at its normal cooling rate. The test sample was then sectioned in half, and visually inspected for any reaction that may have occurred in the refractory resulting from contact with the packing sand and metal. The phase changes in the packing as a result of the high temperature heat treatment were examined by X-ray diffraction.

RESULTS AND DISCUSSION

TESTS AT 1570°C

The results of several cup tests, conducted at 1570°C (2860°F) for 45 minutes, are shown in Fig. 1. At this temperature there was no dissociation of either zircon packing material, nor any indication of other than superficial reaction between the zircon and any of the refractories. Both classes of mullite showed some reaction, near the top of the cups, where there was contact between metal and refractory material, most evident in the phosphate bonded mullite (MPB). The results for the two spinel compositions and for periclase (not shown) were similar in all respects to those shown for alumina (AT2D).

Both the zircon sand and the Borefil were resistant to wetting and penetration by the molten metal, which can be seen as a button on top of the zircon in several of the pictured cups. Whether there would be infiltration of molten metal under the considerable pressure exerted by the mass of metal in the ladle cannot be determined by this test method. If so, this could be expected to be more severe with the Borefil, where the apparent porosity and the pore sizes are greater.

The zircon sand partially sintered to form a cylindrical pellet of low strength, was easily broken between the fingers. Sintering was accompanied by a considerable shrinkage, which in practice would result in exposure to molten metal of the upper portion of the nozzle. The Borefil, on the other hand, showed little if any shrinkage and partial sintering occurred only at grain contact points: the agglomerated mass is readily friable and is considered unlikely to cause any restriction of the nozzle.

TESTS AT 1716°C

The results of tests at 1716°C (3120°F) confirmed that the zircon sand and Borefil dissociated to form a silica-rich liquid phase and a crystalline zirconia, as predicted by the phase diagram data.

The phosphate bonded mullite cup in contact with metal and zircon sand for 45 minutes at 1716°C suffered severe degradation, illustrated in Fig. 2. In the reacted zone, mullite and monoclinic zirconia were identified by X-ray diffraction. Clearly, the liquid phase derived from dissociation of the zircon penetrated the grain boundaries of the refractory cup, reacting with the excess alumina of the matrix and in the grain boundaries (remnant of the phosphate bonding), to ultimately form mullite and precipitate zirconia on cooling. Neither class of mullite-based refractories is suited to exposure to zircon at this temperature.

The extent of attack on the aluminas, spinels and periclase samples resulting from contact with zircon sand-metal and Borefil-metal at 1716°C for 45 minutes is shown in Fig. 3 and 4. Again, at this temperature, the zircon sand and the Borefil dissociated to form ZrO_2 and a siliceous liquid phase, which then penetrated into the refractories along the grain boundaries and reacted with the matrix materials of the refractories.

It is evident that the silica-rich liquid phase dissolved both classes of alumina, leading to the ultimate crystallization of mullite. The reaction products of the zircon packing materials alone would consist of

cristobalite and cubic and monoclinic zirconia at room temperature. X-ray diffraction analysis confirmed the presence of the zirconias, but showed the complete absence of cristobalite in favour of reaction-formed mullite.

For basic refractories such as the spinels and periclase in contact with the zircon materials at the above temperature, the residual products of the packing materials are cubic and monoclinic zirconia, while the silica melt resulting from the dissociation of the zircon reacted with the MgO in the periclase and the spinels to form forsterite (Mg_2SiO_4).

In all tests at 1716°C the residuals of cubic and monoclinic zirconia from the zircon sand sintered into a very hard, compact cylindrical pellet inside the interior hole of the test crucible. The decomposition products from the Borefil material tested at the same temperature retained some of the original texture and showed no such compact sintering effect. It may be concluded that the sintering effect observed in the zircon sand could cause clogging of the ladle nozzle if it adhered to the nozzle wall, or possible blockage of the subsequent slide gate or assorted shrouds and nozzles.

CONCLUSIONS

At normal teeming temperature (1570°C, 2860°F) little or no reaction occurs between the zircon packing materials and any of the refractory materials examined. The Borefil material appears the preferable choice as it sinters to a lesser degree with little shrinkage, whereas the high shrinkage of the zircon sand would expose the upper portion of the nozzle to contact with metal.

It is conceivable that the nozzle may be exposed to further elevated temperatures during superheating of the ladle contents under oxygen blowing. The critical temperature range is considered to be above 1676 to 1687°C (3050 to 3070°F), which respectively mark the dissociation temperature of zircon and the first appearance of a highly siliceous liquid phase that is aggressive towards both alumina and magnesia. Both classes of mullite based refractories were virtually destroyed in contact with zircon above this temperature range; the residues from the packing materials comprise crystalline zirconia. Again, Borefil appears to be the material of choice as the zirconia residue retains the essential structure

of the zircon precursor and would continue to protect the nozzle, whereas the zirconia residue of the zircon sand shrinks markedly as it sinters into a compact lump, exposing the upper portion of the nozzle to the metal and posing a potential threat of blockage within the nozzle or the ensuing system.

REFERENCES

1. Chein, Y.T., Pan, H.C. and Ko, Y.C. "Preparation and performance of packing sands for sliding-gate systems for steel ladles"; Ironmaking and Steelmaking 9:252-257; 1982.

2. "Phase diagrams for ceramists, 1969 supplement"; E.M. Levin, C.R. Robbins and H.F. McMurdie, Eds., American Ceramic Society; 1979.

Table 1. Chemical composition of the refractories

	MES	MPB	AT2D	HIAPB	Zedmag 500	Zedmag 700	Magnesia
Al_2O_3	70.0	71.2	96.0	97.6	33.0	21.1	--
SiO_2	27.5	24.4	3.5	--	2.7	3.5	--
Fe_3O_4	--	--	--	--	5.6	--	--
Fe_2O_3	0.8	0.8	--	--	0.2	3.0	--
TiO_2	1.6	1.6	--	--	--	--	--
MgO	--	1.9	--	1.9	49.0	62.1	99.0
Cr_2O_3	--	--	--	--	1.0	1.0	--
Alkalies	--	--	--	--	1.0	1.0	--
Others	0.1	0.1	0.5	0.5	--	--	--

*MES = Regular mullite, MPB = Phosphate-bonded mullite, AT2D = Ethyl silicate-bonded alumina, HIAPB = Phosphate-bonded alumina, Zedmag 500 = Spinels, Zedmag 700 = Spinels, 6. Magnesia.

Table 2. Composition of the stainless steel

Element	Mass %
Cr	11.0
Mn	0.5
Si	0.5
Ti	0.18
Fe	87.82

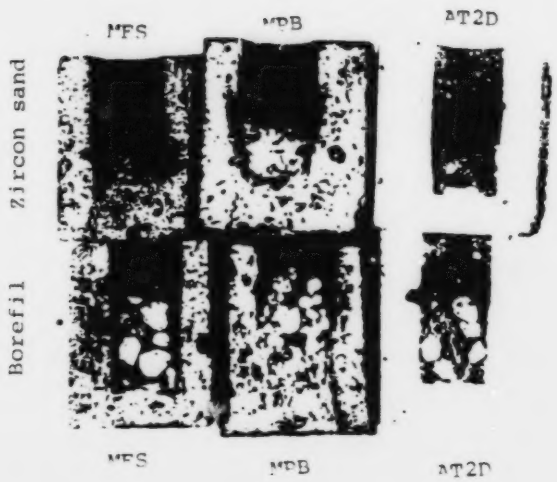

Fig. 1. Showing the performance of refractory materials in contact with zircon sand and Borefil material at 1570°C for 45 min.

Fig. 2. Showing deformation of the mullite nozzle material in contact with zircon sand at 1716°C for 45 min.

Fig. 3. Showing the performance of refractory materials in contact with Borefil packing material at 1716°C for 45 min.

Fig. 4. Showing the performance of refractory materials in contract with zircon sand at 1716°C for 45 min.